

Description

Background of the Invention

[0001] This invention relates generally to the field of photoresists. In particular, this invention relates to the field of photoresists having improved stripping properties, especially suitable for use in printed wiring board manufacture.

[0002] Photoresists are photosensitive films used for transfer of images to substrates. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask to a source of activating radiation. The photoresist has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist-coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

[0003] A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or cross-link in a reaction between a photoactive compound and polymerizable agents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For positive-acting photoresists, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble.

[0004] In general, photoresist compositions include at least a resin binder component, a monomer and a photoactive agent. A wide variety of polymers or resin binders may be used in photoresists. Such polymeric binders may include, as polymerized components, one or more acid functional monomers such as acrylic acid or methacrylic acid. For example, U.S. Patent No. 5,982,153 (Lunney et al.) discloses photoimageable compositions containing polymeric binders having sufficient acid functionality to render the photoimageable composition developable in alkaline aqueous solution. U.S. Patent No. 4,657,865 (Ido) discloses polyacrylic acids used to form polymerizable ester derivatives with ethylenically unsaturated compounds. Such polymerizable ester derivatives are used to form the polymeric binders for photoimageable compositions.

[0005] Monomers useful in photoresist compositions are any which are cross-linkable. Such monomers cross-link to form a polymerized network, having a very large, i.e. infinite, molecular weight. The polymeric binders do not participate in such cross-linking. Rather, the monomers form a polymerized network around the polymeric binders. Typically, polymeric binders contain pendant groups, such as carboxylic acids that react with the developer to increase the water solubility of the binder. Thus, in the unexposed portion, the acid functional polymer is sealed in the alkaline solution, while in the exposed area (protected by the cross-linked monomers), the polymer is not affected. During stripping, the polymerized network (or cross-linked monomer) is attacked or degraded by the stripper allowing it to be removed, whereas the polymeric binder remains relatively unaffected by such strippers.

[0006] Photoresists may be either liquid or dry film. Liquid photoresists are dispensed on a substrate and then cured. Dry film photoresists are typically laminated to a substrate. Such dry film photoresists are particularly suitable for use in printed wiring board manufacture. One problem with conventional dry film photoresist compositions is that they are difficult to strip from electrolytically plated circuit boards using conventional alkaline aqueous stripping solutions; e.g. 3% sodium hydroxide solution. This problem arises from the demand of circuit board manufacturers to reduce the size of printed circuit boards, while increasing their functional capabilities. Consequently, the circuit lines and spaces on the circuit boards have continued to shrink, as more circuitry needs to be accommodated in smaller spaces. At the same time, metal plating heights have also increased above the thickness of the photoresist. This causes the metal to hang over the photoresist, resulting in a very narrow space containing the photoresist being virtually encapsulated by the overplated metal. The photoresist then becomes trapped by the plated overhang, making it difficult to attack and strip by conventional methods. If the photoresist is not completely stripped or removed, rugged copper circuit lines will result after etching which are unsuitable as they can cause short circuiting of the board.

[0007] Some circuit board manufacturers have tried thicker photoresists to accommodate the increasing plating heights, however, this approach is more expensive and limits resolution of the circuit lines. Typically, organic-based (amine- or organic solvent-containing) alkaline stripping solutions are used which produce a smaller stripped particle to facilitate stripping. While such organic-based strippers remove the resist better, they are expensive relative to inorganic-based strippers (e.g. sodium or potassium hydroxide) and have more waste treatment and environmental concerns associated with them. Solvent-soluble photoresists are much less desirable due to workplace regulations limiting or prohibiting solvent emissions.

[0008] Certain polymer binders have been described optionally containing one or more multifunctional monomers, optionally copolymerized with another monomer, including certain multifunctional monomers. The multifunctional monomers disclosed are tri- or tetra-functional (meth)acrylates, esters or relatively low molecular weight, i.e. typically ≤ 450 , difunctional (meth)acrylates esters. Polymer binders containing such tri- and tetra-functional monomers or such rela-

therely low molecular weight difunctional (meth)acrylate esters suffer from gel formation, which makes such polymers

unsuitable for use in photorealist compositions.

Summary of the Invention

1001-01 It has been surprisingly found that branched blends polymers including branch-point monomers as polymerized units provide photostabilizable compositions having improved stability or removability. It has also been surprisingly found that such branch-point monomers as polymerized units do not adversely affect other properties of the

photoreactive composition such as chemical resistance. Further, it has been found that the present branched binder polymers are not subject to gel formation.

19 In one aspect, the present invention provides a photocurable composition including a branched polyimide binder, a monomer and a photocatalytic component, wherein the branched polyimide binder includes as polymerized units one or more difunctional branch-point monomers having two polymerizable end groups and a backbone including one or

[0072] In another aspect, the present invention provides a method of manufacturing a printed wiring board including more basic cleavable functionalities provided that if the diunctional branch-point monomer is free of urethane linkages and both polyimideable end groups are (meth)acrylate esters the diunctional branch-point monomer has a molecular weight of 2450.

25 the steps: a) disposing on a printed writing board substrate a photoreactive composition including a branched polymeric binder, a monomer and a photoactive component, wherein the branched polymeric binder includes as polymerized units one or more difunctional branch-point monomers having two polymerizable and groups and a backbone including one or more base cleavable functionalities, provided that if the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters the difunctional branch-point monomer has a molecular weight of 450; b) imaging the photoreactant; c) developing the photoreactant.

[0013] In a further aspect, the present invention provides a method or forming a relief image including the steps of: a) disposing on a printed writing board substrate a photoresist composition including a branched binder, a monomer and a photoactive photoinitiator, wherein the branched polymeric binder includes as polymerized units one or more difunctional branch-point monomers having two polymerizable end groups and a backbone including one or more base

cleavable functionalities, provided that if the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters the difunctional branch-point monomer has a molecular weight of

2-450; b) imaging the photoresist; and c) developing the photoresist. [0014] In a still further aspect, the present invention further provides a compound having the formula A-Z-B, wherein A and B each include one or more polymericizable groups and Z includes one or more base cleavable groups, wherein the compound has a molecular weight of 2-450.

Detailed Description of the Invention

[1015] As used throughout this specification, the following abbreviations shall have the following meanings, unless the context clearly indicates otherwise: °C = degrees Centigrade; g = grams; mg = milligrams; mJ = millijoules; μ m =

micron = micrometer; T_g = glass transition temperature; °F = degrees Fahrenheit; wt% = percent by weight; and mil = 0.001 inch.

[0041] The terms "resin" and "polymer" are used interchangeably throughout this specification. The term, "alkyl" refers to linear, branched and cyclic alkyl. The terms "halogen" and "halo" include fluorine, chlorine, bromine, and iodine.

Thus the term "halogenated" refers to fluorinated, chlorinated, brominated, and iodinated homopolymers and copolymers and include dimers, trimers, oligomers and the like. The term "(methyl)acylate" refers "polymers" refer to both

to both acrylate and methacrylate. Likewise, the term "methacrylic" refers to both acrylic and methacrylic. "Monomer" refers to any ethylenically or acrylenically unsaturated compound capable of being polymerized. As used throughout this specification, the term "branch-point monomer" refers to any compound containing two or more segments of this specification, the term "branch-point monomer" refers to any compound containing two or more segments of

groups and having one or more base cleavable functionalities in its backbone disposed between the two or more polymerizable groups. "Difunctional branch-point monomer" refers to a branch-point monomer having only two polym-

ortable end groups, i.e. two end groups that are polymerized into the binder polymer backbone. A "branched" polymer refers to a polymer having an interconnected network, such as interconnected to form a three-dimensional network;

but having a finite molecular weight. The terms "cross-linker" and "cross-linking agent" are used interchangeably throughout this specification. The terms "printed wiring board" and "printed circuit board" are used interchangeably

throughout this specification. A "pendant group" refers to any group suspended from a polymer, i.e. only one end of the group is attached to the polymer. Such pendant group is not part of the backbone of the polymer. All numerical ranges (e.g.) All percentages are percent by weight and all ratios are by weight, unless otherwise noted. All numerical ranges

are inclusive and combinable in any order, except where it is obvious that such numerical ranges are constrained to add up to 100%.

[0016] The photore sist compositions of the present invention include a branched polymeric binder, a monomer and a photoactive component, wherein the branched polymeric binder includes as polymerized units one or more difunctional branch-point monomers having two polymerizable end groups and a backbone including one or more cleavable functionalities provided that if the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylates esters, the difunctional branch-point monomer has a molecular weight of ≥ 450 . In an alternative embodiment, the present invention provides a photore sist composition including a branched polymeric binder, a monomer and a photoactive component, wherein the branched polymeric binder includes as polymerized units one or more difunctional branch-point monomers having a backbone including one or more urethane linkages and one or more base cleavable groups.

[0017] A wide variety of polymeric binders are suitable for use in the present invention. Suitable polymeric binders are those containing as polymerized units one or more ethylenically or acrylenically unsaturated monomers and one or more difunctional branch-point monomers having two polymerizable end groups and a backbone including one or more base cleavable functionalities, provided that if the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylates esters the difunctional branch-point monomer has a molecular weight of ≥ 450 . Suitable ethylenically unsaturated monomers include, but are not limited to: (meth)acrylic acid, (meth)acrylates, alkyl (meth)acrylates, alkyl (meth)acrylate, aromatic (meth)acrylates, vinyl aromatic monomers, nitrogen-containing compounds and their heteroanalogues, substituted ethylenic monomers, cyclic olefins, substituted cyclic olefins and the like. Preferred monomers include (meth)acrylic acid, alkyl (meth)acrylates and vinyl aromatic monomers.

[0020] Typically, the alkyl (meth)acrylates useful in the present invention are $(C_1-C_{20})alkyl$ (meth)acrylates. Suitable alkyl (meth)acrylates include, but are not limited to, "low cut" alkyl (meth)acrylates, "mid cut" alkyl (meth)acrylates and "high cut" alkyl (meth)acrylates.

[0021] "Low cut" alkyl (meth)acrylates are typically those where the alkyl group contains from 1 to 6 carbon atoms. Suitable low cut alkyl (meth)acrylates include, but are not limited to: methyl(meth)acrylate, methyl acrylate, ethyl acrylate, propyl(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)acrylate, cyclohexyl(meth)acrylate, cyclohexyl(meth)acrylate, cyclohexyl acrylate and mixtures thereof.

[0022] "Mid cut" alkyl (meth)acrylates are typically those where the alkyl group contains from 7 to 15 carbon atoms. Suitable mid cut alkyl (meth)acrylates include, but are not limited to: 2-ethylhexyl acrylate ("EHA"), 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, decyl(meth)acrylate, isooctyl(meth)acrylate (based on branched $(C_6-C_{12})alkyl$ isomer mixture), undecyl(meth)acrylate, dodecyl(meth)acrylate, tridecyl(meth)acrylate, tetradecyl(meth)acrylate, hexadecyl(meth)acrylate (also known as myristyl(meth)acrylate), pentadecyl(meth)acrylate and mixtures thereof. Particularly useful mixtures include dodecyl-pentadecyl(meth)acrylate, a mixture of linear and branched isomers of dodecyl, tridecyl, tetradecyl and pentadecyl(meth)acrylates; and lauryl-myristyl(meth)acrylate.

[0023] "High cut" alkyl (meth)acrylates are typically those where the alkyl group contains from 16 to 24 carbon atoms. Suitable high cut alkyl (meth)acrylates include, but are not limited to: hexadecyl(meth)acrylate, heptadecyl(meth)acrylate, octadecyl(meth)acrylate, nonadecyl(meth)acrylate, decyl(meth)acrylate, octyl(meth)acrylate and mixtures thereof. Particularly useful mixtures of high cut alkyl (meth)acrylates include, but are not limited to: octyl-decyl(meth)acrylate, which is a mixture of hexadecyl, octadecyl, decyl and dodecyl(meth)acrylate, and caprylic-stearyl(meth)acrylate, which is a mixture of hexadecyl and octadecyl(meth)acrylate.

[0024] The mid-cut and high-cut alkyl (meth)acrylate monomers described above are generally prepared by standard esterification procedures using technical grades of long chain aliphatic alcohols, and these commercially available alcohols are mixtures of isobutyls of varying chain lengths containing between 10 and 15 or 16 and 20 carbon atoms in the ester group. Examples of these alcohols are the various Ziegler catalyzed AL-FOL alcohols from Vista Chemical Company, i.e., ALFOL 1618 and ALFOL 1620, Ziegler catalyzed various NEOOL alcohols from Shet Chemical Company, i.e., NEOOL 25, and naturally derived alcohols such as Proctor & Gamble's TA-1616 and CO-1270. Consequently, for the purposes of this invention, alkyl (meth)acrylate is intended to include not only the individual alkyl (meth)acrylate product named, but also to include mixtures of the alkyl (meth)acrylates with a predominant amount of the particular alkyl (meth)acrylate named.

[0025] The alkyl (meth)acrylate monomers useful in the present invention may be a single monomer or a mixture having different numbers of carbon atoms in the alkyl portion. Also, the (meth)acrylamide and alkyl (meth)acrylate monomers useful in the present invention may optionally be substituted. Suitable optionally substituted (meth)acrylamide and alkyl (meth)acrylate monomers include, but are not limited to: hydroxy(C_2-C_{12})-alkyl (meth)acrylates, di-alkylamino(C_2-C_{12})-alkyl (meth)acrylates, di-alkylamino(meth)acrylates, di-alkylamino(C_2-C_{12})-alkyl (meth)acrylates.

[0026] Particularly useful substituted alkyl (meth)acrylate monomers are those with one or more hydroxyl groups in the alkyl radical, especially those where the hydroxyl group is found at the β -position (2-position) in the alkyl radical. Hydroxymethyl (meth)acrylate monomers in which the substituted alkyl group is a (C_2-C_{12})-alkyl, branched or unbranched,

are preferred. Suitable hydroxyl(methyl)acrylate monomers include, but are not limited to: 2-hydroxyethyl methacrylate, "HEMA", 2-hydroxyethyl acrylate, 1-methacryloyloxy-2-hydroxyethyl methacrylate.

Yeast, 2-hydroxy-propyl Acetate, 1-methyl-2-hydroxyethyl Acrylate, 2-hydroxybutyl Acetate and mixtures thereof.

thi-1-phenyl-3-oxobutyl) methacrylamide, N-methacrylamide of amioethoxy ethylene urea, N-methacryloyloxy ethyl morpholine, N-maleimide of dimethylaminopropylamine and mixtures thereof.

[0028] Other substituted (methacryloyl) monomers useful in the present invention are silicon-containing monomers

(meth)acrylate, vinyl trif(C₁-C₄alkoxy) (meth)acrylate, 2-propylsuccinolactone (meth)acrylate and mixtures thereof. [0029] The vinyl aromatic monomers useful as unsaturated monomers in the present invention include, but are not limited to: styrene, hydrostyrene, α -methylstyrene, vinyltoluene, ρ -methylstyrene, ethylvinylbenzene, vinylisopropylbenzene, and mixtures thereof. The vinylicene monomers also include their corresponding substituted

counterparts, such as halogenated derivatives, i.e., containing one or more halogen groups, such as fluorine, chlorine or bromine, and nitro, cyano, $(C_1-C_6)alkoxy$, $halo(C_1-C_6)alkyl$, carb($C_1-C_6)alkylamino$,

(603) The nitrogen-containing compounds and their thio-analogues useful as unsaturated monomers in the present invention include, but are not limited to: vinylpyridines such as 2-vinylpyridine or 4-vinylpyridine; (C₁-C₆alkyl substituted no derivatives and the like.

N-vinyl pyridines such as 2-methyl-5-vinyl-pyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinyl-pyridine, and 2-methyl-3-ethyl-5-vinylpyridine; methyl-substituted quinolines and isoquinolines; N-vinylcapro-

pyrrolidone, 4-methyl-1-vinyl-pyrrolidone, 5-methyl-1-vinyl-pyrrolidone, 3-ethyl-1-vinyl-pyrrolidone, 3-butyl-1-vinyl-pyrrolidone, 3,3-dimethyl-1-vinyl-pyrrolidone, 4,5-dimethyl-1-vinyl-pyrrolidone, 5,5-dimethyl-1-vinyl-pyrrolidone, 3,3,5-tri-

are not limited to: vinyl acetate, vinyl formamide, vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, vinylidene fluoride, vinylene bromide, tetrafluoroethylene, trifluoroethylene, trifluoromethyl vinyl acetate, vinyl ethers and

clotadienes, norbornene, maleic anhydrides and the like. Such cyclic olefins also include spirocyclic olefin monomers such as spirocyclic norbornenyl monomers, spirocyclic cyclohexene monomers, spirocyclic cyclopentene monomers

alkylamino, C_1-C_6 alkylamino, C_1-C_6 alkylalkylamino, C_1-C_6 alkylcarbonyl, C_1-C_6 alkylalkylcarbonyl, C_1-C_6 alkylalkylcarbonyl, and the like. Particularly suitable substituted cyclic olefins include maleic anhydride (C_6-C_8),

and cyclic olefins containing one or more of hydroxy, alkoxy, $\text{C}_1\text{-C}_6$ alkyl, carbonyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ alkylcarboxyl, $\text{C}_1\text{-C}_6$ alkoxycarbonyl, $\text{C}_1\text{-C}_6$ alkylhydroperoxy, and carbonyl. It will be appreciated by those skilled in the art that the above and all other substituents may be optionally substituted such as with halogen, hydroxyl, or

(C₁-C₆alkoxyl, mercapto, (C₁-C₆alkylthio, amino, acid, thiole, leaving group and the like. Suitable carbon(C₁-C₆alkoxy substituents include, but are not limited to, those of the formula C(O)O-LG, wherein LG is a leaving group including,

but are not limited to, alkyl groups having 4 or more carbon atoms with at least one quaternary carbon atom bonded directly to a carboxylate oxygen such as *tert*-butyl esters, 2,3-dimethylbutyl esters, 2-methylpentyl esters, 2,3,4-tri-

binder polymers of the present invention provided that such branch-point monomers contain a backbone comprising one or more base cleavable functionalities or moieties, and provided that if the functional group or groups are disposed between the polymerizable groups of the branch-point monomer, and provided that if the functional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters, the difunctional branch-point monomer has a molecular weight of ≥ 450 . By "base cleavable functionality" is meant any functionality or group that can be cleaved by a base such as hydroxide ion, alkoxide ion, ammonia, amines, and the like.

[0034] A wide variety of difunctional branch-point monomers containing base cleavable moieties may be used in the present invention. In general, such branch-point monomers have the structure

A-Z-B

[0035] "Substituted alkyl" refers to any alkyl group having one or more of its hydrogens replaced by another substituent group selected from halo, cyano, hydroxyl, (C₁-C₆)alkylamino, di(C₁-C₆)alkylamino, phenyl, and carboxylic acid(C₁-C₆)alkyl, and the like. "Substituted alanyl" refers to any alanyl group having one or more of its hydrogens replaced by another substituent group selected from halo, cyano, hydroxyl, (C₁-C₆)alkylamino, amino, (C₁-C₆)

photocrosslinkers, may provide improved flexibility and be particularly useful in conformal photoresist formulations. The choice of such spacer groups will depend upon the particular use of the polymer photoresists. Spacers having extended chain length may also provide improved flexibility and be particularly useful in conformal photoresist formulations. The choice of such spacer groups will depend upon the particular use of the polymer photoresists.

ferred that the difunctional branch-point monomers contain 2 or more bases cleavable groups and still more preferably 3 or more base cleavable groups. Particularly suitable difunctional branch-point monomers contain 4 base cleavable

groups, and more particularly 4 or more ester linkages. It is further preferred that the difunctional branch point monomer contain as polymerizable end groups monolayers that also contain one or more base cleavable linkages, such as (methacryloyl) esters. When the difunctional branch point monomer contain 2 or more base cleavable linkages, such as

groups may be directly bonded to each other or may be separated by one or more spacer groups. An exemplary structure for such branch-point monomers having multiple base cleavable groups is

BCG22 refer to base cleavable groups 1 and 2, respectively, $x_1 + x_2 + x_3 = 0-20$, and for B, B₁, BCG₁ and B₂ as defined above. Other suitable structures having more or fewer spacers and/or base cleavable groups or different configurations

[0028] Suitable difunctional branch-point monomers useful in preparing the branched binder polymers of the present

hal-ppg425-hdi-ppg220-hdi-ppg425-hdi->shem, shem->hd-ppg1000-hdi-ppg220-hdi-ppg1000-hdi->shem, shem->hd-ppg220-hdi-ppg425-hdi->shem, and shem->hd-ppg1000-hdi-ppg220-hdi-ppg1000-hdi->shem. In the above described diurethane branch-point monomers, each "dash" represents a urethane group (formed when an isocyanate group reacts with a hydroxy group) between the adjacent isocyanates. Such urethane linkages are not required in the present branch-point monomers. The abbreviations for the isocyanates are: hd = 1,6-hexamethylene diisocyanate; popc200 = TONE® Polyol 0200 Diol (containing carbonylic ester groups); popc201 = TONE® Polyol 0201 Diol (containing carbonylic ester groups); popc220 = TONE® Polyol 0220 Diol (contains carbonylic ester groups); ppopc25 = polypropylene glycol having a molecular weight of approximately 425; ppg1000 = polypropylene glycol having a molecular weight of approximately 1000; cmpa = dimethylolpropionic acid; pmb = 3-sopropenyl-alpha, alpha-dimethylbenzyl isocyanate; 2hema = 2-hydroxyethyl methacrylate (contains ester group and a polymerizable end group); ethem = ethoxylated hydroxyethyl methacrylate (contains ester group and a polymerizable end group); and enic14 = ethoxylated caprolactone-derived methacrylate (contains ester groups and a polymerizable end group). Such branch-point monomers are generally commercially available or may be readily prepared by known methods. TONE® is a trademark for polycaprolactone diols, available from the Dow Chemical Company (Midland, Michigan). Other suitable polycaprolactone diols are available from Sovay under the CAPA brand name. Typically, the molecular weight of the branch-point monomers is 2450, and preferably from 2400 to 6000.

[lower] The branched polymer contains one or more present functional groups as poly(methacrylate) or one or more functional branch-point monomers having two polymethylene and groups and a backbone including one or more base cleavable functionalities, provided that if the difunctional branch-point monomer is free of urethane linkages and both polymerizable and groups are (meth)acrylate esters the difunctional branch-point monomer has a molecular weight of ≥ 450 .

Wilton polymeric binders are prepared from: i) terp. or higher-functional branch-point monomers, ii) those containing 3 or more polymeric end groups, such polymeric binders are much more likely to suffer from gel formation, which makes such binders unsuitable for use in photore sist compositions. Further, when polymeric binders are prepared from

containing low molecular weight, i.e. 2×450 , diunctional branch-point monomers containing no urethane linkages and containing polymeric esters as both polymerizable end groups, such polymeric binders also suffer from gel formation. Such gel formation is not problem when the diunctional branch-point monomers are of higher molecular weight,

[0040] The present invention further provides a compound having the formula A-Z-B wherein A and B each include one or more methacrylate groups.

more than one functional branch-point monomer may be present in a polymer chain. The term *branch-point monomer* may be used to describe a monomer which contains one or more polymerizing groups and 2 includes one or more base cleavage groups, wherein the compound has a molecular weight of 450.

35
monomers may advantageously be used in the present invention. Thus, the total amount of such difunctional branched-point monomers in the branched binder polymers is from 0.1 to 100 weight percent, based upon the total weight of the monomers used in preparing the branched binder polymers and, in preference, from 1 to 50 weight percent.

use to prepare and understand, however, may not be so wide, and more probably, will not be so wide. The branched binder polymers of the present invention may be prepared by a variety of methods known in the art, such as free radical polymerization.

40 **Photocatalytic compositions may include one or more polymeric binders. Such mixtures of binder polymers can be photopolymerized to form one or more branched binder polymers or one or more branched binder polymer combined with one or more unbranched binder polymers. The number polymers may be mixed or blended in any suitable ratio. The anticorrosion inhibitor may be included in any suitable ratio.**

dependent upon the specific binder polymers employed, whether they are branched or unbranched, and the specific properties desired. Such retics are within the ability of one skilled in the art. It is further understood that the structural and mechanical characteristics of the polymers contain sufficient end functionality in

render the binder polymers soluble and removable upon development. The term "acid functionality" refers to any tune ionizable carboxylic acid group, such as carboxylic acid, anhydride, and ester groups, and to any functional group capable of forming a salt upon contact with alkaline developer, such as dilute alkaline aqueous sodium or potassium borohydride, at 1 to 3 weight percent. Suitable acid functionality includes, but is not limited to carboxylic acid, carboxylic anhydride, and ester groups.

acids, sulfonic acids, phosphonic acids and phenols. In general, the binder polymers have an acid number of up to 100, sulfonic acids, phosphonic acids and phenols, in general, have an acid number of up to 200. Typical ranges of acid numbers are from 15 to 250 and preferably from 50 to 250. Such acid numbers are based on the amount of KOH (monobasic potassium borate) in mg to neutralize 1 g (dry weight) of the polymer.

of binder polymer.

Typically, the photoinitiator is present in the photomagnetic compositions in an amount of up to 80 wt%, based on the total weight of the composition, preferably from 20 to 80 wt%, more preferably from 25 to 95 wt%, and even more preferably from 30 to 80 wt%.

Substituted hydrophobic trihalomethyl containing photore sist strip enhancers include a wide variety of compounds containing a trihalomethyl group which hydrolyzes to carboxylate anions during stripping of the photore sist. Preferably, such hydrophobic trihalomethyl containing photore sist strip enhancer is alpha-trichloromethyl benzyl acetate. Such optional additives will be present in various concentrations in a photore sist composition. For example, filters and dyes may be used in relatively large concentrations, e.g. in amounts of from about 5 to 30 percent by weight, based on the total weight of the composition's dry components.

[0053] The photore sist compositions of the present invention are typically prepared by combining the branched polymeric binder, monomer, photoactive component, optional solvent and optional additives in any order.

[0054] Processing of the photore imageable or photore ist compositions of the invention may be in any conventional manner. In a typical procedure, a photore ist layer, either formed from a liquid composition or transferred as a layer from a dry film, is applied to a substrate. When a liquid photore ist composition is used, it may be applied to a substrate by any known means, such as spinning, dipping, roller coating and the like.

[0055] The present photore ist compositions may be used on a variety of substrates used in the manufacture of electronic devices such as printed wiring boards and integrated circuits. Suitable substrates include copper surfaces of copper clad boards, printed wiring board inner layers and outer layers, wafers used in the manufacture of integrated circuits and the like.

[0056] Once the photore ist is applied to the substrate, it is imaged or exposed to actinic radiation through an appropriate artwork. In the case of a negative-acting photore ist, exposure of actinic radiation polymerizes the cross-linking agent in exposed areas, resulting in a cross-linked structure that is resistant to developer. Next, the composition is developed such as by using dilute alkaline aqueous solution. Suitable developers include 1-3 wt% aqueous solutions of sodium hydroxide or potassium hydroxide. Organic based developers, such as triethylbenzylammonium hydroxide based developers, may be used but are less preferred.

[0057] During such development, the acidic groups of the binder polymers form salts which render the binder polymers soluble and removable. An advantage provided by the present polymeric binders is that

[0058] Thus, the present invention provides a method for forming a relief image including the steps of: a) disposing on a printed writing board substrate a photore ist composition including a branched binder, a monomer and a photoactive component, wherein the branched polymeric binder includes units one or more difunctional branch-point monomers having two polymerizable end groups and a backbone including one or more difunctional branch-point monomers, provided that i) the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters; the difunctional branch-point monomer has a molecular weight of ≥ 450 ; b) imaging the photore ist; and c) developing the photore ist.

[0059] In the case of negative-acting photore ist applied to copper surfaces of copper clad boards, an etchant may be used after development to remove copper from those areas where the photore ist was removed, thereby forming a pristine circuit. The remaining resist is then removed using a stripper.

[0060] The present invention further provides a method of manufacturing a printed wiring board including the steps of: a) disposing on a printed writing board substrate a photore ist composition including a branched polymeric binder, a monomer and a photoactive component, wherein the branched polymeric binder includes as polymerized units one or more difunctional branch-point monomers having two polymerizable end groups and a backbone including one or more base cleavable functionalities; and b) disposing on a printed writing board substrate a photore ist composition including a branched polymeric binder, a monomer and a photoactive component, wherein the branched polymeric binder includes as polymerized units one or more difunctional branch-point monomers having two polymerizable end groups and a backbone including one or more base cleavable functionalities; and b) disposing on the printed writing board substrate the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters; the difunctional branch-point monomer has a molecular weight of ≥ 450 to form a photore ist composition; and c) developing the photore ist.

[0061] The present photore ist compositions show enhanced removal as compared to conventional photore ist. Thus, the present invention also provides a method of enhancing the removal of a photore ist composition from a substrate including the step of combining a branched polymeric binder, a monomer and a photoactive component.

[0062] The present photore ist compositions show enhanced removal as compared to conventional photore ist. Thus, the present invention also provides a method of enhancing the removal of a photore ist composition from a substrate including the step of combining a branched polymeric binder, a monomer and a photoactive component, having two polymerizable end groups and a backbone including one or more base cleavable functionalities; provided that i) the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters; the difunctional branch-point monomer has a molecular weight of ≥ 450 to form a photore ist composition; and disposing the photore ist composition of a substrate; imaging the photore ist composition; and developing the imaged photore ist composition. In conventional photore ist, the photore ist is stripped by action of a base on the polymeric monomer network, which is typically cleaved by the base. In conventional photore ist, however, the polymeric binders are at best "eaten" by the base, meaning that pendant acid groups are converted to their corresponding salts, thus improving the water solubility of the binder polymers. While not intending to be bound by theory, it is believed that the present branched polymeric binders are also cleaved by the base used to strip the photore ist, thereby removing the resist by chemical breakdown of the polymer binder as well as by dissolution of the polymer binder.

[0063] It has also been surprisingly found that the present difunctional branch-point monomers used to prepare the present branched binder polymers do not adversely affect other properties of the photore ist binder such as chemical resistance. Thus, the present photore ist compositions also show improved adhesion as compared to conventional

photoresist compositions. Further, the present photoresist compositions show improved, i.e. faster, stripping with substantially no loss of chemical resistance, as compared to conventional photoresist compositions. Typically, as adhesion of a dry film photoresist is improved, the photoresist composition is harder to strip. The present photoresist compositions surprisingly provide both increased adhesion and improved stripping. Additionally, photoresist compositions of the present invention show increased photoresist as compared to conventional photoresist compositions containing pol-

ymeric binders that are not branched.

[0063] The present photoresist compositions are particularly suitable for use when small features are desired, such as least than or equal to 3 mil lines and spaces. Typically, such small features are harder to plate and thus the substrates, such as printed wiring boards, are left in the plating bath longer resulting in overplate. Such overplate makes removal of conventional photorests difficult. An advantage of the present invention is that the photoresist is easily and rapidly removed, even from underneath such overplated metal, as compared to conventional photorests.

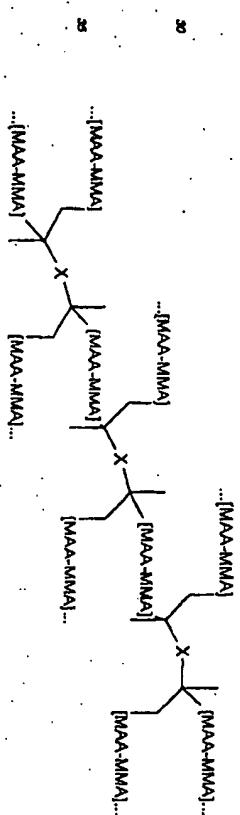
[0064] The following examples are intended to illustrate further various aspects of the present invention, but are not intended to limit the scope of the invention in any aspect.

Example 1

[0065] Two binder polymers were prepared as follows.

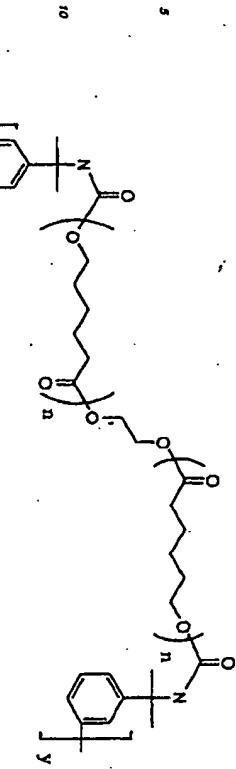
[0066] Comparative Binder: A monomer mixture (25% methacrylic acid, 75% methyl methacrylate) was diluted to 36% by weight with methyl ethyl ketone and then brought to reflux. An initiator was added to initiate the polymerisation reaction. Periodic additions of the initiator were added thereafter until the monomers were polymerized.

[0067] Branched Binder: 1. A monomer mixture of 25% methacrylic acid, 71.5% methyl methacrylate, 3.5% of a moiety containing base cleavable functionalities having the formula $\text{pmbb-}(\text{PPO})_{200}\text{-pmbb}$, where the "dashes" represent urethane linkages was diluted to 36% by weight with methyl ethyl ketone and then brought to reflux. An initiator was added to initiate the polymerization reaction. Periodic additions of initiator were added thereafter until the monomers were polymerized. The resulting branched binder had the generalized structure:



wherein X has the generalized structure:

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and wherein $y = 1$ and $n = 2$. In the above structure, MMA refers to methyl methacrylate and MAA refers to methacrylic acid. The ellipses indicate that the MMA-MAA units are further attached to other MMA-MAA units as well as other branch-point monomers, forming a network having a finite, i.e. not infinite, molecular weight.

Example 2

[0058] Photoresist compositions were prepared by combining the polymer binders from Example 1 (53 wt%), with bisphenol A, 10 ethoxy dimethacrylate monomer (43 wt%), commercially available initiator 1 (3.5 wt%), commercially available initiator 2 (0.05 wt%), green background dye (0.05 wt%), antioxidant (0.2 wt%) and flow additive (0.2 wt%). The above ingredients were mixed to a 50% solids mixture in a 4:1 mixture of methyl ethyl ketone and isopropanol. After mixing for 2 to 4 hours using a lab mixer, the 50% solids mixture was dried on 0.3 mil thick polyester a. approximately 80° C for 3 to 9 minutes. The 50 micron thick dried photoresist (less than 1.0% residual solvents) was then covered with 1.0 mil thick polyethylene forming a package of polyester / resist / polyethylene (finished "dry film").

Example 3

35 [0059] The negative working photoresist composition from Example 2 was hot roll laminated to a cleaned, copper plated panel. The laminated panel were then covered with an artwork (phototool) and imaged with UV radiation using an Optibeam 7100 with enough energy to achieve a copper step 9 using a Stouffer 21 Step Wedge. After exposure, the polyesther sheet was removed and the resist was then developing in 1% sodium carbonate monohydrate at 30° C. In the development process, the unexposed resist was removed. After development, the remaining (exposed) lines were examined for defects. The smallest lines with no defects and with 400 microns spaces were recorded as the fine line addition. Smaller lines are more easily attacked in the developing solution and thus by the conveyor equipment, thus a lower number indicates better adhesion. After examining the developed lines, the panels were then plated in a copper sulfate electrolytic plating bath until the resist height (50 microns) was exceeded by 20% (60 microns of plating). The exposed resist was then stripped from the panel with 3% sodium hydroxide at 50° C. The resulting lines (or the complete removal of the photoresist) were recorded. The results are reported in Table 1.

Table 1

Sample	Photocatal for Copper Step 9	Fine Line Adhesion	Step Time
Comparative	77 mJ	33 μ m.	28.2 sec
1	65 mJ	27 μ m.	18.5 sec

[0070] It can be clearly seen from these data that photoresist compositions of the present invention have improved

adhesion, increased photospeed and reduced stripping time as compared to conventional photoresists.

Example 4

[0071] Other suitable branched binder polymers were prepared according to Example 1. These polymers are reported in Table 2 in terms of the monomers used to prepare the polymers.

Table 2

[0072] All amounts in Table 2 are reported in percent by weight of the total weight of monomers used to prepare the polymer. The branch-point monomers ("BPM") used were: BM1 = methacrylic anhydride; BM2 = pentyl-PePo20-PePo20; BM3 = pentyl-PePo20-pentanol; and BM4 = ethAc14-hdi-PgP-1000-hdi-Et14. The conventional monomers ("CM") used were: CM1 = ethoxylated hydroxymethyl methacrylate; CM2 = ethAc14; CM3 = methacrylic acid; CM4 = methyl methacrylate; and CM5 = *n*-butyl acrylate.

[0073] The procedure of Example 1 was repeated using monomers containing one or more base cleavable groups.

having (meth)acrylate ester as the polymerizable groups and having a molecular weight of < 450. The monomers used, the amounts and the molecular weights of the monomers are reported in Table 3.

Table 1

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As can be seen from the above data, monomers having (methacrylate ester)s as the polymerizable groups and having a molecular weight of < 450 gelled during the polymerizations. Thus, such monomers are unsuitable for use as branching point monomers in preparing the branched polymers of the present invention.

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1. A photoprotectant composition comprising a branched polymeric binder, a monomer and a photoactive component, wherein the branched polymeric binder comprises as polymerized units one or more difunctional branch-point monomers having two polymerizable groups and a backbone comprising one or more base cleavable functionalities, provided that if the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters the difunctional branch-point monomer has a molecular weight of 62450.

2. The composition of claim 1 wherein the photoactive component is selected from 9-phenylacridine, 1-phenylglycine, benzophenone, N,N-dimethyl-4,4'-diaminobenzophenone, N,N-dimethyl-4,4'-diaminobenzophenone, 4-methoxy-4'-dimethylaminobenzophenone, 3,3'-dimethoxy-4,4'-methoxybenzophenone, p,p'-bis(dimethylaminobenzophenone), p,p'-bis(dimethylaminobenzophenone), antrquinone, 2-ethylanthraquinone, naphtquinone, naphthoquinone, benzophenone, benzal, benzylmethylether, benzolmethylether, benzolisopropenylether, benzol-1-butyl, benzophenoneether, methylbenzoin, ethylbenzoin, dibenzyl, benzodiphenylsulfide, benzylmethylketone, 1,7-bis-(2-ethylphenyl)heptane, 2-chlorotetraamine, 2-methyltetraamine, 2,4-dimethyltetraamine, 2,4-dimethylhexanone, 2-isopropylthioxanthone, 1,1-dichloroacetoacetone, p-t-butylidochloro-acetoacetone, 2,2-dichloroacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-dichloro-4-phenoxycetophenone, 2-(o-chlorophenyl)-4-(o-chlorophenyl)methacrole dimer, 2-(o-chlorophenyl)-4,5-difluorophenyl imidazole dimer, 2-(o-chlorophenyl)-5-styreneimidazole dimer, 2-(o-methoxyphenyl)-4,5-difluorophenyl imidazole dimer, 2-(o-methoxyphenyl)-5-(2-phenylmethyl)imidazole dimer, 2,4-difluorophenylphenyl-5-phenylimidazole dimer, 2-(2,4-dimethoxyphenyl)-

4,5-diphenylimidazole dimer, 2-(p-methoxymercaptophenyl)-4,5-diphenylimidazole dimer and mixtures thereof.

3. The composition of any one of claims 1 to 2 wherein the polymeric binder comprises sufficient acid functionality to render said photoreimageable composition developable in alkaline aqueous solution.

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4. The composition of any one of claims 1 to 3 wherein the polymeric binder has an acid number of from about 50 to about 250.

10 5. The composition of any one of claims 1 to 4 wherein the one or more base cleavable functionalities are selected from anhydrides, esters, carbonates, or sulfonyl esters.

6. The composition of any one of claims 1 to 5 wherein the branched polymeric binder comprises from 0.1 to 25 w%

20 of one or more branch-point monomers, based upon the total weight of monomers in the polymeric binder.

15 7. The composition of any one of claims 1 to 6 wherein the difunctional branch-point monomers comprise 2 or more base cleavable groups.

8. The composition of any one of claims 1 to 7 wherein the monomer is selected from methyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, n-hexyl acrylate, methyl methacrylate, hydroxymethyl acrylate, butyl methacrylate, octyl acrylate, 2-ethoxyethyl methacrylate, 1-butyryl acrylate, 1,5-pentanediol dicrylate, N,N-diethylaminomethyl acrylate, ethylene glycol dicrylate, 1,2-propanediol dicrylate, decamethylene glycol dicrylate, decamethylene glycol dimethacrylate, 1,4-cyclohexanediol dicrylate, 2,2-dimethylolpropano dicrylate, glycerol dicrylate, tripropylene glycol dicrylate, glycerol triacrylate, 2,2-(4-hydroxyphenyl)propane dicrylate, triethylene glycol dicrylate, 1,9-propoxypropoxytrimethylolpropane tricrylate, ethylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2-dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol trimethacrylate, 1,2,4-trimethyl-1,3-pentanediol dimethacrylate, pentamethylol trimethacrylate, 1-phenyl ethylene-30 acrylate, 1,4-benzenediol dimethacrylate; styrene, substituted styrene, vinyl toluene, vinyl esters and mixtures thereof.

9. A method of manufacturing a printed writing board comprising the steps of: a) disposing on a printed writing board substrate a photorecast composition of any one of claims 1 to 8.

35 10. A method for forming a relief image comprising the steps of: a) disposing on a printed writing board substrate a photorecast composition of any one of claims 1 to 8.

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